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THE USE OF THIN LAYER CHROMATOGRAPHY  
FOR THE DETERMINATION OF ANTIOXIDANTS  
IN VULCANIZED RUBBER

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Foreign Technology Division  
Wright-Patterson Air Force Base, Ohio

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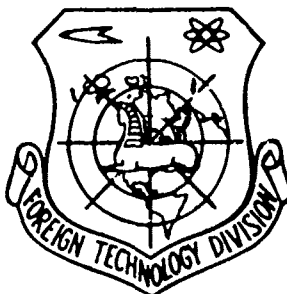
## FOREIGN TECHNOLOGY DIVISION



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VULCANIZED RUBBER

by

G. M. Solodova, A. I. Malyshev,  
and Ye. Ye. Postovtseva



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13. ABSTRACT  
Neozor (phenyl-beta-naphthylamine), 4010NA (4-phenylene-N-1-isopropenyl-p-phenylenediamine), and p-hydroxynozon (p-hydroxy-phenyl-beta-naphthylamine) antioxidants were sepd. by thin layer chromatog. on silica gel using 1:0:5:0.1 of a given formula. The spots were scraped from the plate, and the antioxidants were extd. with hot etoh and analyzed spectroscopically (less than 10% error) after treatment with a certain diazotized oxidizing mixt.  
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## EDITED TRANSLATION

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By: G. M. Solodova, A. I. Malyshev, and  
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# U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

\* ye initially, after vowels, and after ъ, ь; e elsewhere.  
 When written as ѣ in Russian, transliterate as ye or e.  
 The use of diacritical marks is preferred, but such marks  
 may be omitted when expediency dictates.

## THE USE OF THIN LAYER CHROMATOGRAPHY FOR THE DETERMINATION OF ANTIOXIDANTS IN VULCANIZED RUBBER

G. M. Solodova, A. I. Malyshev, and  
Ye. Ye. Rostovtseva

Antioxidants are added to unvulcanized and vulcanized rubber in order to protect them from the effect of the oxygen of the air and from ozone [1]. The most varied combinations of antioxidants are used in mixtures of one in another. Methods of determining the individual antioxidants and their mixtures are known [2].

In this article a method for the quantitative determination of neozone "A" (phenyl- $\beta$ -naphthylamine), 4010NA (N-phenyl-N-isopropyl-p-phenylenediamine) and p-hydroxyneozone (p-hydroxyphenyl- $\beta$ -naphthylamine) and their combined presence in crude vulcanized rubber mixtures and vulcanizates, is described. Chemical and spectrophotometrical methods for determining these substances in a mixture without their preliminary separation is unsuitable. In an analysis of a pure mixture of the antioxidants (neozone A, 4010NA and p-hydroxyneozone) their quantitative determination using a spectrophotometric method is possible by means of solving a system of equations. However, the presence of softeners and accelerators in the vulcanized rubber which have the same maxima of absorption as the listed antioxidants [3] complicates the analysis. In connection with this a preliminary separation of the antioxidants was made by the method of chromatography using a thin layer of silica gel. The success of this method is well known [4-5].

Following the separation of the antioxidants in the thin layer their identification and quantitative determination was made photo-colorimetrically ( $\Phi\Xi\text{H-M}$ ) and spectrophotometrically ( $\text{C}\Phi\text{-4}$ ), by using calibrated curves plotted based on pure antioxidants. In order to check the method, mixtures of pure antioxidants as well as vulcanized rubber mixtures and vulcanizates were used. The maximum error of the method for a mixture of pure antioxidants amounted to 10%.

**Preparation of the plates with the thin layer of adsorbent.** Seven g of HCH make silica gel, ground and screened through a No. 014 sieve, are mixed with 17 ml of water and the entire thoroughly mixed mass is applied as an even layer on a glass plate, 18 x 14 cm in size.

The plate was dried for 2 hours in air in a steep horizontal position, and then dried at 105°C in a thermostat for 30 min.

**Preparation of the samples of the analyzed vulcanized rubber mixture and vulcanizate.** About 1 g of a thinly sliced vulcanized rubber mixture or vulcanizate is placed in an extraction flask, 30 ml of acetone added and extracted for 30 min in a boiling water bath, and the extract poured into another flask. The weighed sample of extract was then treated with fresh portions of acetone and extracted twice, using 30 ml of acetone each time. The excess of acetone was boiled down to 25 ml.

The obtained solution was analyzed chromatographically.

**Chromatographic analysis of the extract.** From a starting point located 1-2 cm from the edge of the plate, 0.1 ml drops of the analyzed solution and the "check" solutions of standardized materials were applied to the plate 2 cm from one another using a micropipette. The plate was placed in a chromatographical chamber.



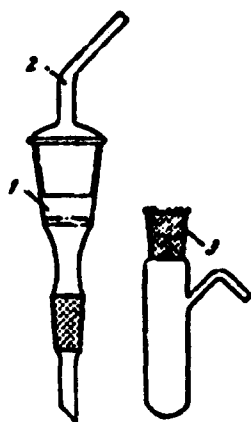
Mixtures of the solvents: benzene, acetone and concentrated ammonia at ratios (100:5:0.1) were used as the moving phase for the separation of the neozone D, 4010NA and p-hydroxynozone.

Following the front advancement of the solvent at a height of 12-15 cm the plate is removed from the chamber and dried slightly in air. Then, the plate is put under an ultraviolet light, and the location of the spots for the analysis is determined, by comparing them with the location of the "check" spots; using the point of a needle or scalpel the identified zone is marked off by the glow of the spots of antioxidants. The values of the antioxidants are presented in Table 1.

Table 1. Values of  $R_f$  and the coloration of the antioxidant in ultraviolet light.

Antioxidant	$R_f$	Coloration
Neozone D	0.84	Bright violet
4010NA	0.73	Brown
p-hydroxynozone	0.42 (I) 0.55 (II)	Pale lilac

The spots encircled with the scalpel were collected in a funnel with a No. 4 glass filter using vacuum (figure).



Device for getting the target zone with a chromatograph. 1 - No. 4 glass filter with a porous bottom (No. 14 sealed ground joint); 2 - T-shaped tube (No. 20 sealed ground joint); 3 - test tube with an outlet (No. 14 sealed ground joint).

The antioxidants were washed from the filter and the silica gel using hot ethyl alcohol, into a test tube with an outlet connected to a jet pump. Each antioxidant was collected in a 25 ml graduated flask for the subsequent colorimetric analysis on a ФЭК-М. Neozone Д and p-hydroxynozone were determined according to their reaction with diazotized para-nitroaniline (raspberry stain) [6], 4010NA - with an oxidizing mixture [7], which is made in the following way:

0.5 g of the oxide of copper acetate, 4.66 g of calcium chloride, 10 ml of 0.5 N hydrochloric acid solution and 250 ml of water were mixed in a 1 l graduated flask, and ethyl alcohol slowly added to the one liter mark.

In analyzing the artificial mixtures by this method, the relative error did not exceed 10%.

The analytical results of several commercial products are given in Table 2.

Table 2. The determination of the concentration (in %) of antioxidants in crude vulcanized rubber mixtures and vulcanizates.

No. of mixture	Antioxidant	Introduced	Found		Relative error	
			I	II	I	II
1	Neozone Д	0.65	0.64	0.64	1.5	1.5
	4010NA	0.65	0.60	0.56	8.0	14.0
	p-hydroxynozone	0.65	0.53	0.47	18.0	27.0
2	Neozone Д	1.25	1.25	1.20	2.4	6.0
	4010NA	1.25	1.10	1.10	14.0	14.0
	p-hydroxynozone	0.65	0.54	0.47	22.0	27.0
3	Neozone Д	1.20	1.37	1.28	6.3	1.5
	4010NA	0.65	0.60	0.58	8.0	11.0
	p-hydroxynozone	0.65	0.55	0.48	11.0	26.0

Remark 1. The relative error in the analysis of the crude vulcanized rubber mixtures (I) and of the vulcanizates (II) in certain cases reaches more than 20%, which can be explained by the incomplete desorption of the antioxidants from the vulcanized rubbers made with carbon black.

Table 2. (Cont'd).

2. The content (in g) of the analyzed mixtures for Nos. 1, 2 and 3, respectively:

Natural rubber.....	100	100	100
Stearin.....	2	2	2
Neozone A.....	1	2	2
4C10NA.....	1	2	1
p-hydroxynéozone.....	1	1	1
Zinc oxide.....	5	5	4
Lamp black.....	40	40	40
Sulfur.....	3	3	3

Aluminum oxide was also used as an adsorbent for the chromatography (TY 2962-54); the thickness of the unattached layer on the plate was 1 mm. Benzene was used for the separation of the mixture. The error of the analysis was the same as in the previous experiments.

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